Magnetism of NaCl type uranium compounds

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Magnetism of NaCl Type Uranium Compounds

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Abstract

The magnetic properties of the actinides are caused by the 5f-electrons. On this background a localized model as well as a band model describing the magnetic properties are presented. The magnetic properties of the NaCl type uranium compounds are summarized with special attention to uranium monophosphide, UP and uranium monosulphide, US.

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Abstract to

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1. INTRODUCTION

After the extensive research that has been carried out on magnetism of the rare earths or the lanthanides, elements Nos. 57 to 71 and their compounds the attention has recently been focused on the actinides, elements Nos. 90 to 103 and their compounds. In fact work has only been done on the first few actinides as the rest of the elements of the series are unstable. The magnetic properties of the lanthanides are due to the 4f-electrons whereas the magnetic properties of the actinides are caused by the 5f-electrons. Therefore the two series of elements have to some extent analogous magnetic properties.

2. MAGNETISM OF NaCl-TYPE URANIUM COMPOUNDS

The NaCl-type uranium compounds with group V and group VI elements have during the last few years been studied in details. More papers on these compounds have been published[1,2,3,4,5] whereas actinide compounds with other crystal structures than the fcc NaCl structure have been delt with less. Here we give a summary of the magnetic properties of uranium compounds with NaCl-structure. In table 1 the properties of the UV-compounds are given and table 2 contains the properties of the UVI-compounds. As are seen there exists a spread in the experimental values obtained from different measurements. There are several causes of these uncertainties. Most experiments as e.g. the susceptibility and magnetization measurements are performed on polycrystals. Impurity and non-stoichiometry of the preparations cause the results to vary from sample to sample. Only few measurements have been performed on sigle crystals by use of the neutron scattering technique - a combination which gives results that are direct in an atomic scale and more accurate.

3. MODELS OF THE MAGNETIC PROPERTIES OF THE UX-COMPOUNDS

3.1. Localized Model

Analogously to the lanthanides, it is assumed as a first approximation model that magnetism of the actinidecompounds is due to the actinide 5f -electrons that are localized. However, the spatial extension of the 5f-wave functions is larger than that of the 4f-wave functions, so the localization of the actinides is poorer than in the lanthanides i.e. the interaction between

the 5f-electrons and the environment is stronger in the actinides than that of the corresponding lanthanides. The former can thus appear at various oxidation states, whereas the layer are known to exist mainly in the trivalent state. It is difficult to decide how many 5f-electrons there are localized in actinide compounds. Curves of susceptibility and magnetic form factors might contribute to calculating the number of localized 5f-electrons. Susceptibility curves show that UV-compounds have a $5f^1$- configuration and UVI-compounds a $5f^2$ - configuration, whereas magnetic form factor curves give a $5f^3$ - configuration for the UV-compounds. However, the uncertainty of these results is large. The remaining electrons form a conduction band which explains the large electrical conductivity of the UX-compounds.

Assuming that the 5f-electrons in the actinide cations are strongly localized and that they obey the Russel- Saunders coupling so J is the good quantum number the actinide ions can be treated by crystal field theory to account for the magnetic moments in the ordered states and the susceptibilities in the paramagnetic states. From Hund's rules we find for the ground states of the different $5f^n$- configurations the total spin angular momentum S, the total orbit angular momentum L and the total angular momentum J, where $\underline{J} = \underline{L} + \underline{S}$. In table 3 the Lande factors g_J, the paramagnetic moments n_p and the saturation moments n have been calculated from the expressions:

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2\,J(J+1)}$$

$$n_p = g_J \sqrt{J(J+1)}$$

$$n = g_J J$$

The magnetic coupling between separated actinide ions is via the Ruderman -Kittel-Kasuya-Yosida mechanism, i.e. an indirect coupling between the magnetic 5f-electrons via the conduction electrons. This is made plausible by the fact that the shortest U-U distances are 3.4 - 4.4 Å in the UX-compounds and the mean radius of the 5f shell is 0.4 - 0.6 Å, why a direct magnetic coupling cannot take place.

3.2. Band Model

A more realistic model for explanation of the magnetic properties of the actinide compounds must be based on the bands of the electronic structure. Adachi and Imoto[6] propose the following model for the uranium compounds:

a) The energy bands comprise broad 7s- and 6d bands and a narrow 5f band, which is further split into a number of sub-bands by the crystalline electric field and spin orbit interaction. The Fermilevel lies within the 5f band, so that UN and UP would both have about one 5f electron and US about two 5f electrons

b) The orbital momentum of the 5f electrons is strongly quenced by the crystalline field, which is an aspect quite different from that of the 4f electrons in rare earth compounds.

c) The energy differences between the ground state and the nearest exited states are relatively small, so that the latter states have a predominant influence on the effective moments.

d) The intra atomic exchange interaction between the localized 5f electrons and the conduction 6d and 7s electrons gives rise to the contribution from these last-mentioned electrons to the magnetic moment.

Fig. 1 shows that after Adachi and Imoto[7] the energy bands of NaCl - type uranium compounds.

4. URANIUM MONOPHOSPHIDE, UP

At room temperature uranium monophosphide, UP, has a face centred cubic rock salt structure(fcc). The lattice parameter is at room temperature $a = 5.588$Å[8,9]. A plot of the lattice parameter vs. temperature is shown in fig. 2; it shows that at about 22K there is a step change in the lattice parameter or a change in expansion coefficient from a positive to a negative value. No structural change is observed. The minimum U-U distance is at room temperature $a_{U-U} = 3.939$Å and the UP-distance is $a_{U-P} = 2.795$[2,10]. A computation of the atomic radii gives for UP $a_U = 0.875$Å and $a_P = 1.920$Å.

Magnetic properties:

Uranium monophosphide is an uranium pnictid. The pnictid group UX(V) (X = N, P, As, Sb and Bi) is antiferromagnetic below certain ordering temperatures, the Neel temperatures. In the high temperature limit they are paramagnetic. In fig. 3 the molar susceptibility is shown after Allbut, Dell, Junkison and Marples[11]. From this curve we deduce that the Neel temperature is $T_N = 125$ K, the Weiss constant $\theta = 30$K and the paramagnetic moment $n_p = 3.652\,\mu_B$. It should be mentioned that susceptibility measurements vary from sample to sample caused by impurity and non-stoichiometry of the preparations. The antiferromagnetism of UP has been investigated by neutron

diffraction measurements[12,13,14]. It has been shown that the ordering is of type AF-I: the magnetic moments are aligned ferromagnetically in each layer, but oppositely in altering layers perpendicular to 001-planes, + - + -, see fig. 4. The chemical and magnetic unit cells are of the same size, but where the chemical cell is cubic, the symmetry of the magnetic cell is tetragonal. These measurements give a Neel temperature at T_N=125 K and show another anomali at T=25 K, near the temperature where the lattice parameter change in a way so the expansion coefficient goes negative, see fig. 5 after Curry[12]. The magnetic structure AF-1 was found to be the same from 4 K to the Neel temperature. The magnetic moment/uranium atom was found by Sidnu et al[13] to be $n_a = 1.72 \mu_B$ from measurements of the magnetic structure factor of UP and the magnetic form factor of the uranium atoms in UP.

Electrical resistivity:
The temperature dependence of the electrical resistivity has been measured in the temperature range from about 70 K to room temperature by Adachi and Imoto[6]; their results are shown in fig. 6. The figure shows that the resistivity of UP has a positive temperature-coefficient up to about 120 K, above which temperature it abruptly changes to a weak negative value. The maximum resistivity agrees well with the Neel point. In the same way as with the susceptibility measurements the resistivity measurements are highly sensible to impurity contents.

5. URANIUM MONOSULPHIDE, US

Uranium monosulphide has at room temperature a face centred rock salt structure(fcc). The lattice parameter at room temperature is a = 5.4847Å[8,9]. When the temperature is lowered the structure changes to rhombohedral at T = 175 K, which is the Curie temperature. A ferromagnetic aligning of the magnetic moments along the 111-direction causes this structure change. The variation of the cell volume with temperature for US is shown in fig. 7 after Marples[9]. The cell volume is used rather than the lattice parameter to allow for the change in interaxial angle. From the figure a change in expansion coefficient is observed at the Curie temperature. It is however positive both below and above T_C. The minimal U-U distance is at room temperature a_{U-U} = 3.880Å and the U-S distance is a_{U-S} = 2.742Å[2,10]. The atomic radii are for US after Albutt and Dell[10] a_U = 0.898Å and a_S = 1.844Å.

Magnetic properties:

Uranium sulphide is an uranium chalcogenid. The chalcogen group UX(VI) (X = O, S, Se and Te) is ferromagnetic below certain ordering temperatures, the Curie temperatures. They are as the pnictides paramagnetic in the high temperature limit. Fig. 8 shows the inverse susceptibility vs. temperature after Chechernikov[15] and from this ferromagnetic susceptibility curve we deduce a paramagnetic Weiss temperature θ = 180 K, a Curie temperature T_C = 200 K and an effective paramagnetic moment $n_p = 2.48 \mu_B$. These values differ from values given elsewhere in literature and show the general tendency that susceptibility measurements vary from sample to sample caused i.a. by impurity problems. The magnetic structure of US has been studied by neutron diffraction by Wedgewood[16] on a single crystal. It is found that US is a simple ferromagnet with the moments lying along the 111-axis, which is the rhombohedral axis. By extrapolating the form factor of uranium in US at 4.2 K to sin θ/θ = 0 the saturation ferromagnetic moment of uranium is found to be $1.70 \mu_B$. To show the differences in results that are obtained by using single crystals or poly crystals and by doing neutron diffraction or magnetization measurements Wedgewood gives the following values of the ferromagnetic moment at 4.2 K in μ_B:

neutron diffraction	magnetization	
single crystal	single crystal	poly crystal
1.70	1.55	1.1

The difference between the two single crystal measurements are due to the contribution of conduction electron polarization to the bulk magnetization, which in US has a negative contribution to the magnetization of the uranium ions. The Curie temperature is found to be T_C = 180 K, a value which does not agree with the Curie temperature calculated from the susceptibility measurements of Chechernikov.

Electrical resistivity:
The electrical resistivity has been measured by Furuya[17] in the temperature range from 100 K to 500 K, fig. 9. A change in the temperature coefficient is observed at about 180 - 200 K, which is in the region of the Curie temperature.

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17) H. Furuya, Japan J. Appl. Phys. 7, 779 (1968)

Table I

Properties of the UY-compounds.

Compound	a_o	U-U	Magnetic	T_N	μ_a	χ_g	χ_M	η_p	θ	T	ρ
UY	Å	Å	Structure	°K	μ_B	10^{-6} cgs-emu		μ_B	°K	°K	μΩ-cm
UN	4.8835	3.450	AF-I	53	0.75	7.7	1960	3.05	-310	T_N	155
	4.890							3.08		300	182
								3.11	-325		160
UP	5.5865	3.939	AF-I	123	1.72	20.4	5487	3.31	3	T_N	300
	5.587			125	1.9			3.56	36	300	224
	5.589			130							
UAs	5.766	4.068	AF-I	128	1.89	19.2	6010	3.54	32	300	238
	5.771				2.13					78	
					1.93					4	
					2.30						
USb	6.1805	4.368		213	2.08	26.4	9500	3.85	95	300	357
	6.191		AF-I	246	2.64					4	
					2.16					78	
UBi	6.364	4490	no grade-ing T>4°K	290		16.5	7380	4.06	115		

References: 1-5

Table II

Properties of the UVI – compounds.

Compound	a_o	U-U	Magnetic Structure	T_c	n_f	χ_g	χ_M	n_p	θ	T	S
UVI	Å	Å		°K	μ_B	10^{-6} cgs-emu		μ_B	°K	°K	μΩcm
US	5.467	3.88	F	178	1.20		4180	222	173	300	350
	5.489			180	1.60	209	4600	225	185	1300	235
	5.489						5667				328
USe	5.710	4.07	F	160.5	1.31	22.5	7133	251	188	80	120
	5.744			187						300	600
	5.750			210						1000	750
UTe	6.151	4.35	F	103	1.10	14.3	5230	284	104	80	1200
	6.163			104				236		300	1500
				123						700	2200

References: 1-5

UO is unstable

Comments to table 1 and table 2

a_o: the lattice constant

U-U: the spacing between adjoning uranium ions

F: ferromagnetic ordering, layers ++++

AF-I: antiferromagnetic ordering, layers +-+-

T_c: Curietemperature, ferromagnetic ordering temperature

T_N: Neel temperature, antiferromagnetic ordering temperature

n_f: magnetic moment/U-atom in the ferromagnetic state

n_a: magnetic moment/U-atom in the antiferromagnetic state

n_p: magnetic moment/U-atom in the paramagnetic state

χ_g: the mass susceptibility

χ_M: the molar susceptibility

θ: the Weiss constant

ρ: the specific heat

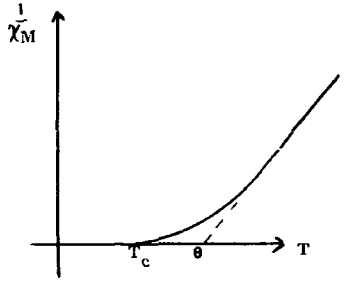
Most of the charactheristic constants are shown in the schematic figures below for the ferro- and the antiferromagnetic susceptibility curves.

The mass- and the molar susceptibility are related through the equation:

$$\chi_M = m\chi_g$$

m is the molar weight of the compound.

1) Ferromagnet

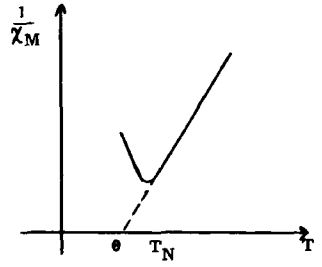


$$\chi_M = \frac{C_M}{T - \theta} \quad ; \quad T \rangle T_c$$

$$n_p = \sqrt{\frac{3K_B}{\mu_B^2 N_{av}} C_M} = 2.829 \sqrt{C_M} = 2.829 \sqrt{\chi_M (T - \theta)} \quad \text{(Bohr magnetons)}$$

K_B: Boltzmanns const.; μ_B: the Bohr magneton; N_{av}: Avagadros number

2) Antiferromagnet

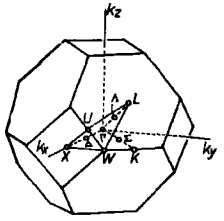


$$\chi_M = \frac{C_M}{T + \theta} \quad ; \quad T \rangle T_N$$

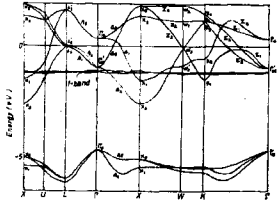
$$n_p = 2.829 \sqrt{\chi_M (T + \theta)} \qquad \text{(Bohr magnetons)}$$

Table 3
The $5f^n$ - configurations of the actinides.

n	1	2	3	4	5	6	7	8	9	10	11	12	13	14
J	5/2	4	9/2	4	5/2	0	7/2	6	15/2	8	15/2	6	7/2	—
g_J	6/7	4/5	9/11	3/5	2/7	0	2	3/2	4/3	5/4	6/5	7/6	8/7	—
n_p	2535	3578	3618	2683	0.845	0	7.937	9.721	10.646	10.607	9.581	7.561	4.536	—
n_s	2.143	3.200	3.273	2.400	0.714	0	7.000	9.000	10.000	10.000	9.000	7.000	4.000	—



Brillouin zone for face-centered cubic lattice



Energy bands of NaCl type uranium compounds

Fig 1

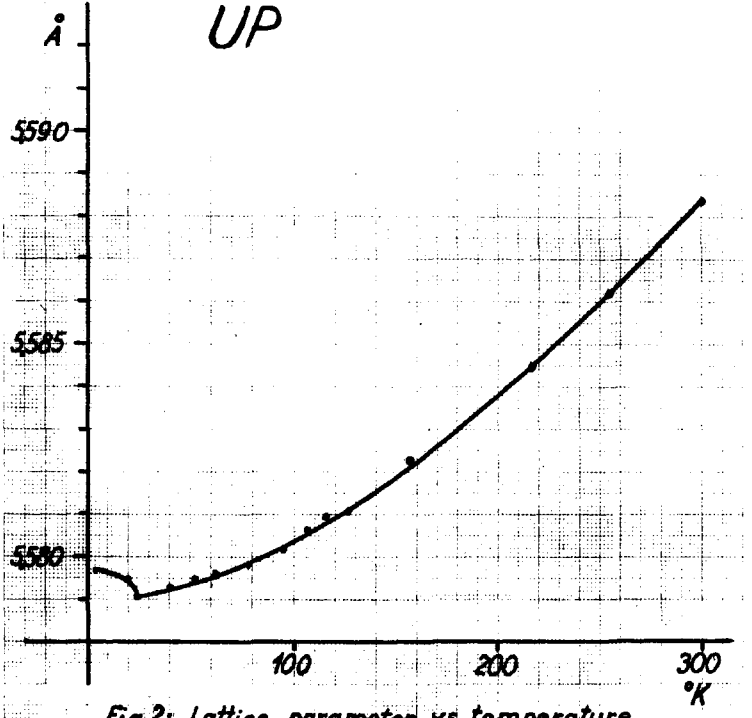


Fig 2: Lattice parameter vs temperature

Reference: J.A.C. Marples, J. Phys. Chem. Sol. 31, 2431, (1970)

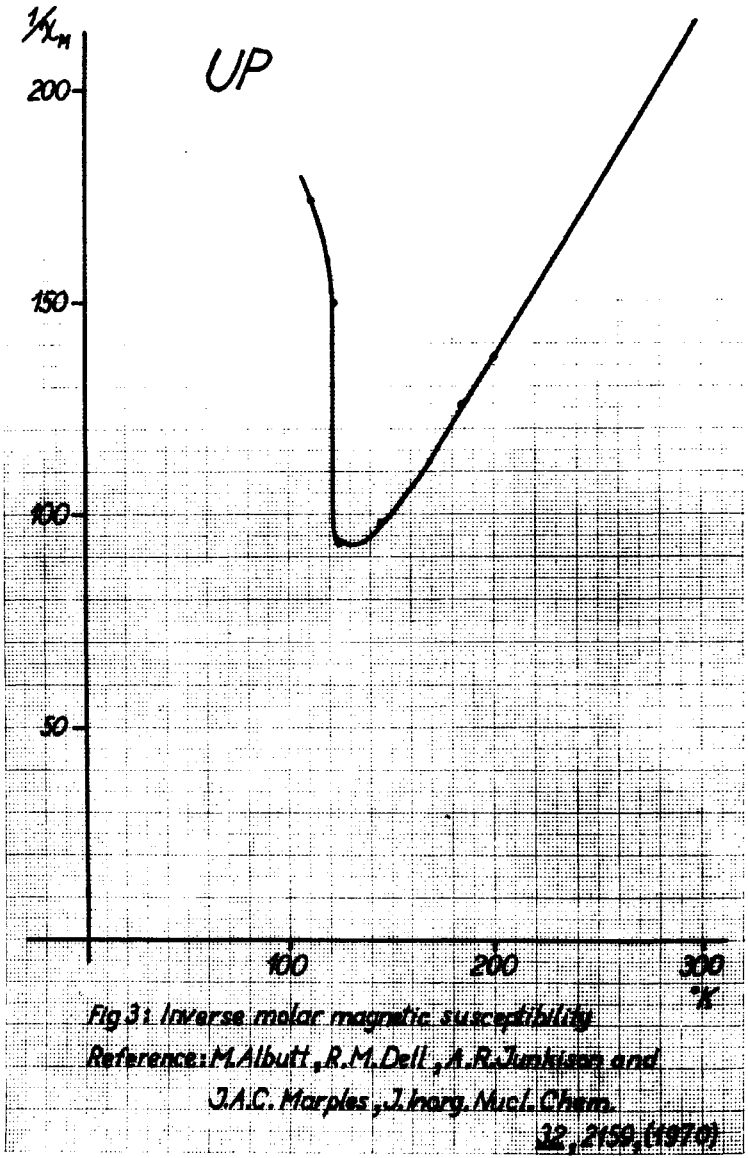
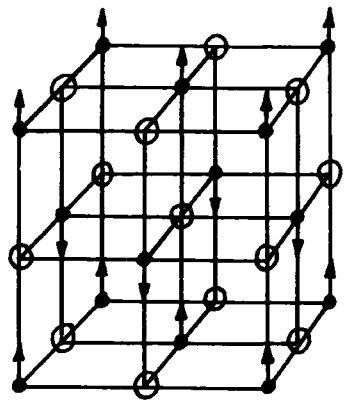


Fig 3: Inverse molar magnetic susceptibility
Reference: M.Albutt, R.M.Dell, A.R.Junkison and J.A.C. Marples, J.Inorg.Nucl.Chem. 32, 2159, (1970)



• uranium
O phosphorus

Fig 4: Antiferromagnetic ordering

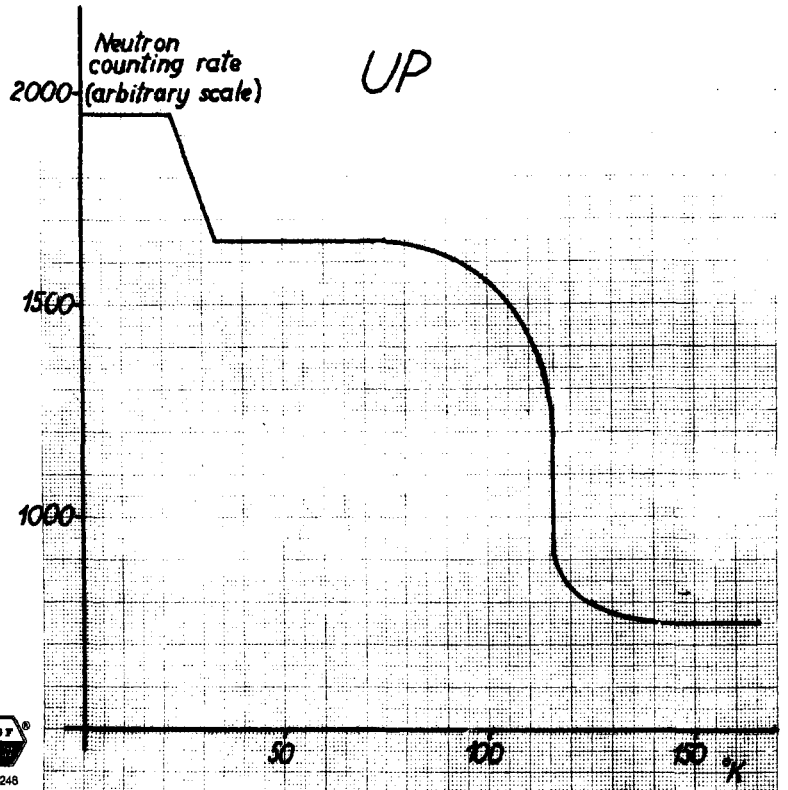


Fig.5 : The temperature variation of the intensity of the 110 magnetic reflection.

Reference : N.A.Curry, Proc.Phys.Soc.,89,427,(1966)

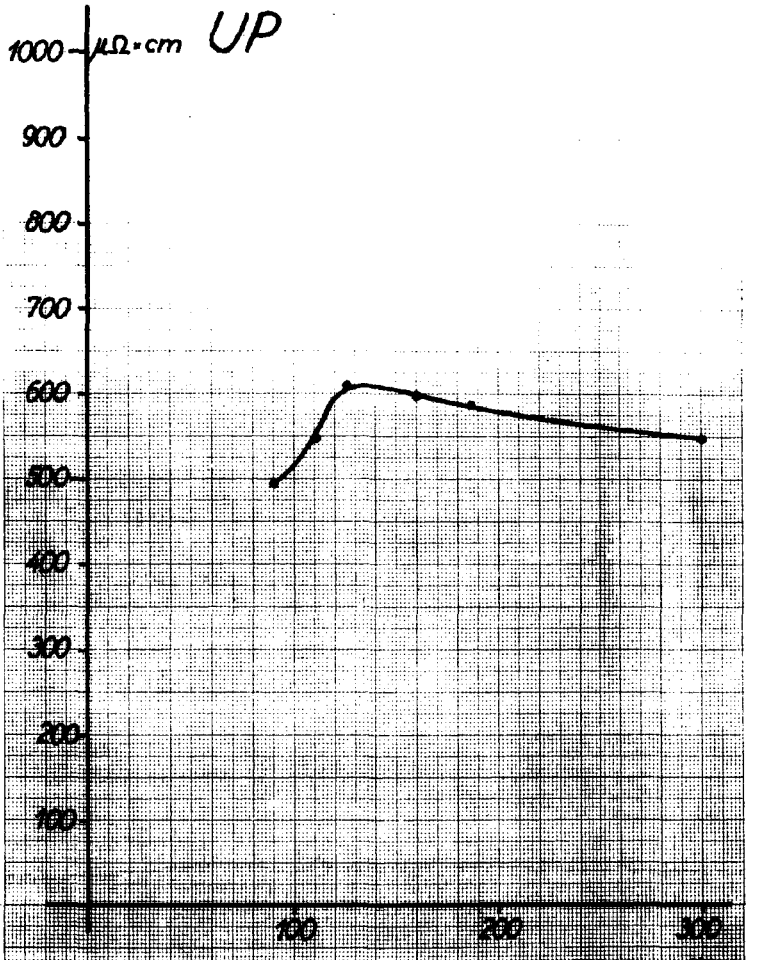


Fig.6 : Electric Resistivity vs Temperature

Reference: H.Adachi and S.Imoto, J.Nucl. Sci. and Tech., 6, 531, (1969)

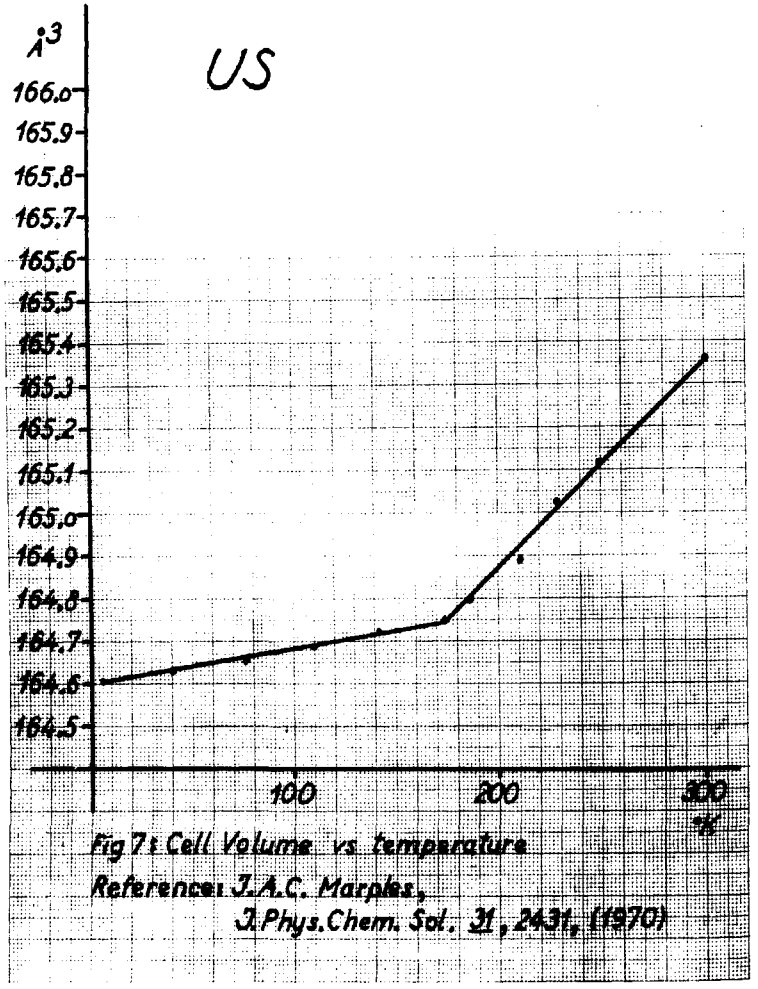


Fig 7: Cell Volume vs. temperature
References: J.A.C. Marples,
J. Phys. Chem. Sol. 31, 2431, (1970)

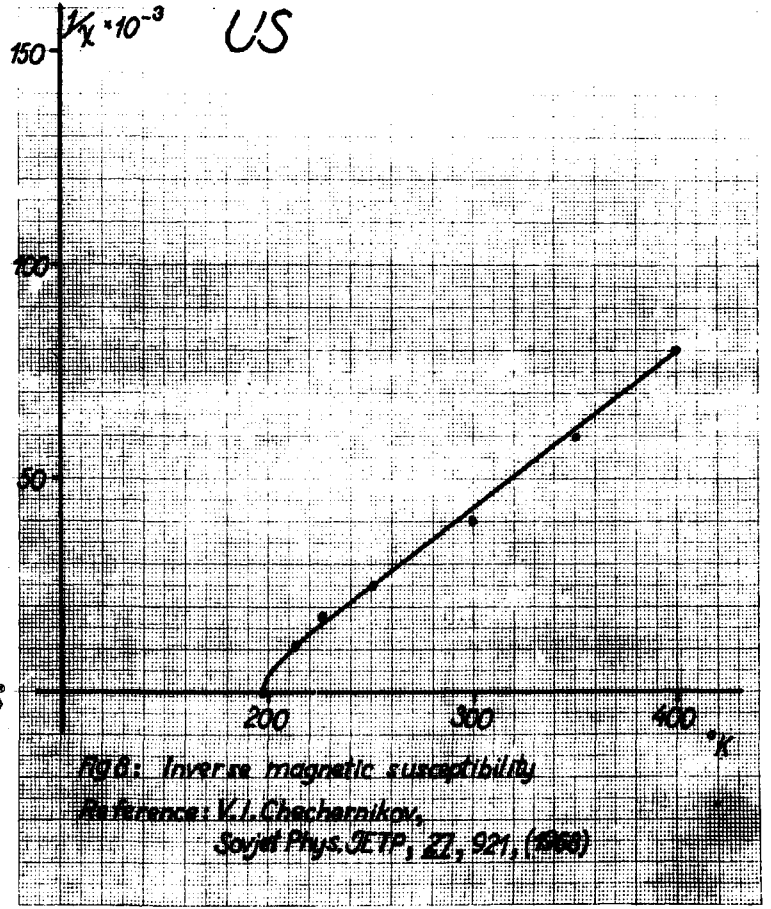


Fig 8: Inverse magnetic susceptibility
Reference: V.I. Chechernikov,
Soviet Phys. JETP, 27, 921, (1968)

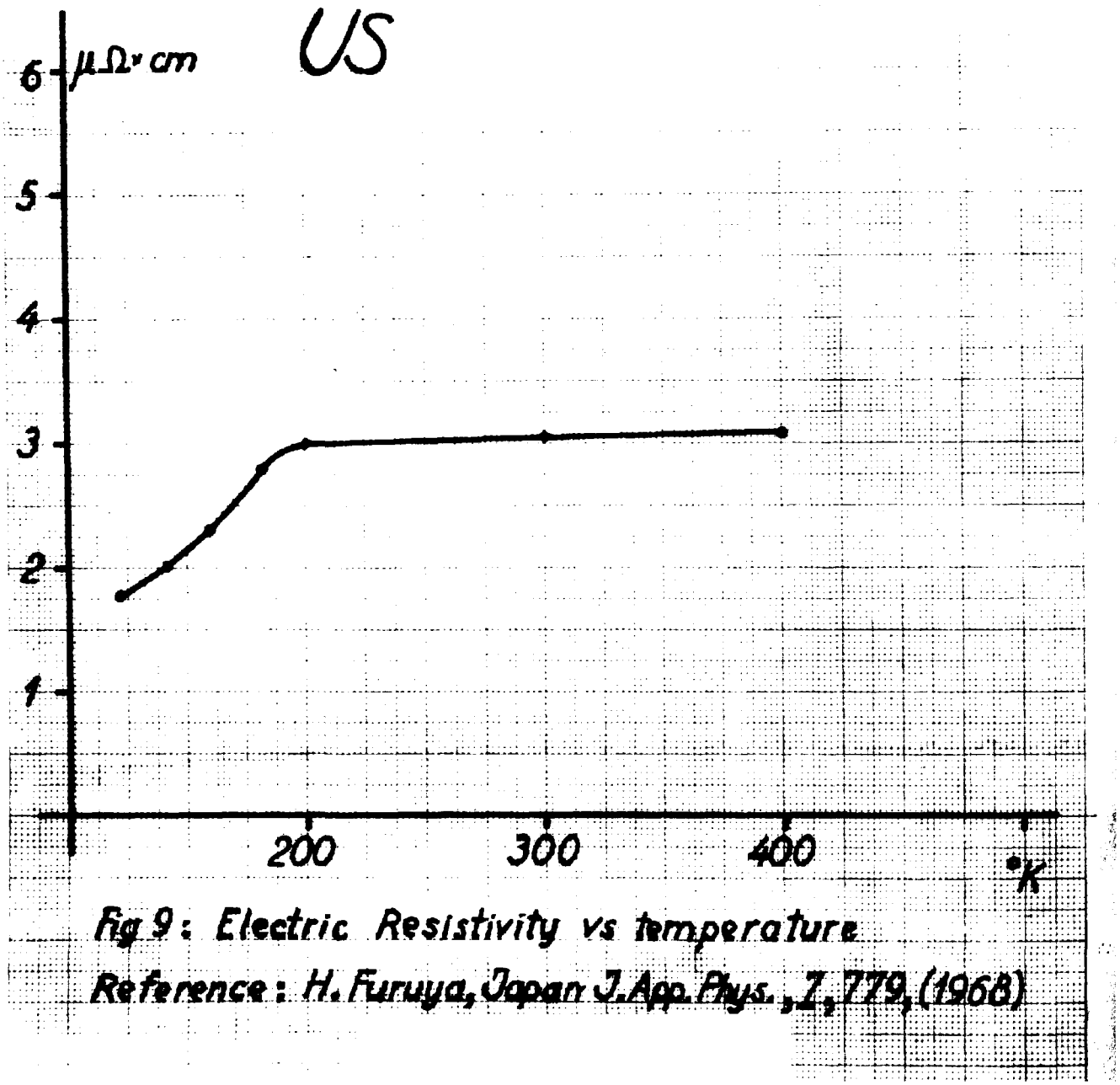


Fig 9 : Electric Resistivity vs temperature

Reference : H. Furuya, Japan J. App. Phys., 7, 779, (1968)